# A GENERAL DEFINITION OF AXIAL, EQUATORIAL AND

RELATED TERMS FOR SUBSTITUENTS ON RINGS OF ANY SIZE

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Summary: A general definition is proposed for substituent positions at a tetracoordinated atom in a ring of any size. The definition is based on the *local environment only* of that atom and is consistent with current usage. It is simpler and more chemically significant than Cremer's nomenclature, which is based on the entire ring.

The definition of *axial* and *equatorial* in the chair conformation of saturated carbocyclic six-membered rings is well defined and does not pose any problem.[1] The presence of hetero atoms such as oxygen, nitrogen and even sulfur is readily accommodated because the ring geometry in the chair is only slightly perturbed. In six-membered rings that exist in the half-chair conformation, such as cyclohexene or cyclohexene oxide, these terms are also satisfactory for the 4 and 5 positions, but the 3 and 6 positions have somewhat different orientations and the terms *pseudoaxial* and *pseudoequatorial* are generally used.[1,2] These terms are simple and can be employed to describe conformational features in many important cyclic and polycyclic molecules, such as terpenes and steroids. However, the situation is more complex in six-membered boat and twist-boat conformations or with other ring sizes.
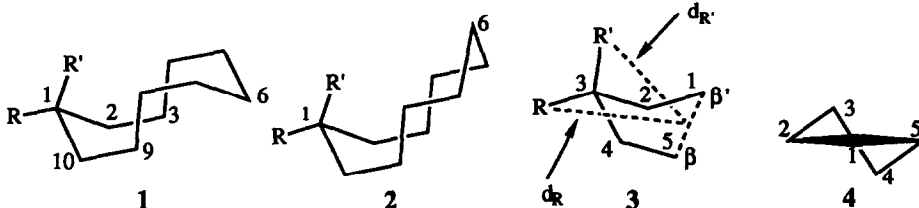
Cremer[3a] has proposed a nomenclature for ring substituent positions based on the Cremer-Pople[3] description of ring puckering which involves the concept of a *mean ring plane*, but this proposal does not seem to have received wide acceptance in organic chemistry. This scheme involves *all* the atoms in a ring, irrespective of its size. For example, in the cyclodecane conformations (1 and 2), a distant atom such as C-6 has virtually no effect on the local environment of C-1, but the mean plane used to define the substituent positions at C-1 depends on the coordinates of C-6. Because the essential difference between the equatorial and axial positions in cyclohexane is the presence of a (steric) interaction between axial substituents on 1:3 related ring atoms, it is sufficient to consider a *five-atom chain in the ring* with the substituent on the central atom, i.e., C-9, C-10, C-1, C-2, and C-3 of 1 or 2.

Consider the distances (d_R and $d_{R'}$) between R and R' at a ring atom (C-3) and the mid-point of the line joining the end atoms (i.e., β and β') of the five-atom ring fragment (C-1 to C-5) in 3. Because the bond lengths, C-R and C-R' can be different, d_R and $d_{R'}$ are calculated for fixed bond lengths of 1.1 Å. The ratio of d_R to $d_{R'}$, where $d_R > d_{R'}$ is then an index (D_{ae}) of the difference in the environments of the two positions. When D_{ae} is 1, R and R' are isoclinal and

a C_2 axis passes through the ring atom. For D_{ae} less than ca 1.05, but not 1 by symmetry, the substituents are nearly isoclinal, as at C-2 in 1. For D_{ae} greater than ca 1.05, R is "axial" and R' is "equatorial" with these terms being used in a rather generalized way. For D_{ae} = ca 1.1 to 1.15, the prefix pseudo can be used to qualify axial and equatorial. A "normal" axial-equatorial site has D_{ae} = 1.2 to 1.3. In the [333] form of cyclononane, D_{ae} (1.55) at the side positions is significantly larger than this normal value because the axial hydrogens actually point inward into the ring. The definitions of d_R and $d_{R'}$ given above can be applied to linear chains and to three- and four-membered rings. In the latter case the β and β' atoms are the same. For fused or bridged systems the ring under consideration may need to be specified. Table I gives a list of D_{ae}'s in a variety of rings.[4] Approximate D_{ae}'s are easily obtained with a ruler and molecular models, and can readily be estimated by a quick look at a model, i.e., the definition is user-friendly!

The definitions given above are satisfactory for ring sizes up to 12, but beyond that size it is possible to have adjacent torsional angles that are close to 180°. Substituents on a carbon flanked by such torsional angles, as in the middle atom on the long side of the [3434] conformation of cyclotetradecane, are isoclinal by the proposed definition. However, one position is clearly inside the ring, whilst the other is outside, and the ring is not large enough for this difference to be meaningless. The definition of D_{ae} given above can be generalized so that 1,4 instead of 1,3 interactions are selected, and the symbols $^{1,3}D_{ae}$ and $^{1,4}D_{ae}$ can then be used (plain D_{ae} being equivalent to the former term). More discussion and an extensive list of D_{ae} values will be presented in a fuller paper.

Table I. D_{ae} Values and Position Labels in Various Rings

Ring and position(s)	$D_{ae}{}^a$	Labels[b]
(4) C_2 cyclopentane, 1	1.00	I, I
2 and 5	1.13	ψa, ψe
3 and 4	1.19	a, e
chair cyclohexane	1.24	a, e
twist-boat cyclohexane	1.00	I, I
	1.28	a, e
half-chair cyclohexene, 3 and 6	1.13	ψa, ψe
4 and 5	1.27	a, e
[333] cyclononane, corner	1.00	I, I
side	1.55	a, e
(1) [2323] cyclodecane, 1, 6	1.47	a, e
2, 5, 7, 10 (corner)	1.03	I, I
3, 4, 8, 9	1.69	a, e

^{a} Ratio of d_R to $d_{R'}$. ^{b} a = axial; e = equatorial; ψ = pseudo; I = isoclinal.

References and Notes

1. Eliel, E. L.; Allinger, N. L.; Angyal, S. J.; Morrison, G. A. *Conformational Analysis*, Interscience: New York, 1965, p 36.

2. Anet, F. A. L. in *The Conformational Analysis of Cyclohexenes, Cyclohexadienes, and Related Hydroaromatic Compounds*; Rabideau, P. W., Ed.; VCH Publishers: New York, 1989; Chapter 1.

3. (a) Cremer, D. *Isr. J. Chem.* **1979**, *20*, 12-19. (b) Cremer, D.; Pople, J. A. *J. Am. Chem. Soc.* **1975**, *97*, 1354-1358. (c) Essén, H.; Cremer, *D. Acta Crystallogr. Sect. B* **1984**, *40*, 418-420 .

4. A modified version (Anet, F. A. L.; Anet, R. *Tetrahedron Lett.* **1985**, *26*, 5355-5358) of the DELPHI program (van de Graaf, B., Baas, J. M. A. *J. Comput. Chem.* **1984**, *5*, 314-321) was used with the MM2 force field (Burkert, U., Allinger, N. L. *Molecular Mechanics*; American Chemical Society: Washington, 1982) in conjunction with the MOL program to give a listing of the D_{ae} values for a given conformation automatically.